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RHEOLOGICAL PROPERTIES OF BOROSILICATE GLASSES AND MELTS

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The effect of concentration and structural factors on the character of the temperature dependence of the viscosity of glasses in the systems K_2O–B_2O_3–SiO_2 and Na_2O–B_2O_3–SiO_2 in the range $10^9 – 10^4$ Pa · sec is determined. It is shown that the effect of boron and potassium oxides on the temperature dependence of the viscosity near the transition from the liquid into the plastic state is complex.

Key words: borosilicate glass, optical fiber, viscosity, index of refraction, linear thermal expansion coefficient.

The system R_2O–B_2O_3–SiO_2 is the base for developing low-index glasses used as light-reflecting and protective cladding for rigid optical fibers.

Glass for the cladding of rigid optical fiber must meet a host of requirements. Of importance together with optical and thermal characteristics are the rheological properties, which must be matched with those of the glass used for the optical fiber core.

To ensure stable drawing of single- and multistrand optical fibers as well as high quality of fiber-optic articles obtained based on them the temperature range of viscosity variation from 10^{10} to 10^4 Pa · sec for glass with a light-reflecting cladding must be at least 360 °C, and the viscosity of the glass used for the cladding must be higher than that of the glass used for the optical fiber core in the range 650 – 1100°C.

Studies of the production of glass for the optical fiber core of rigid optical fibers with improved technological characteristics are described in [1, 2]. The results of these studies made it necessary to develop glass compositions for optical fiber cladding.

The absence of published systematized data on the rheological properties of glasses in the systems K_2O–B_2O_3–SiO_2 and Na_2O–B_2O_3–SiO_2 in the range $10^9 – 10^4$ Pa · sec predetermined the synthesis and study of glass with quite wide ranging compositions, including the following (molar content, %[3]): 65 – 80 SiO_2, 10 – 25 B_2O_3 and 10 – 25 R_2O (Fig. 1).

The experimental glasses were synthesized in a gas-fired batch furnace at maximum temperature 1500°C. The results of gradient heat-treatment of the experimental glasses for 3 h in the temperature range 600 – 1100°C are reflected in Fig. 1. Glass in the system Na_2O–B_2O_3–SiO_2 has a greater tendency to crystallize. The glassy state of borosilicate glass becomes less stable with increasing silicon oxide content.

The physical-chemical characteristics of the synthesized glasses are presented in Table 1. The refractive index was determined by the immersion method. The linear thermal ex-

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[3] The molar content is given here and below.

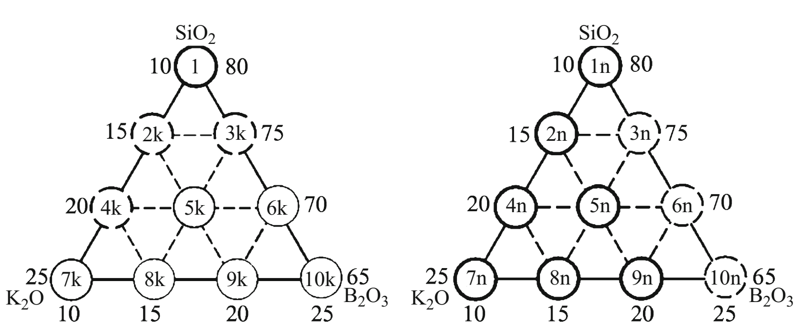

Fig. 1. Glass compositions in the system R_2O–B_2O_3–SiO_2. The results of gradient heat-treatment:) crystalline crust;) crystalline film;) glass with no indication of crystallization. The numbers in the figure show the molar content of the oxides.

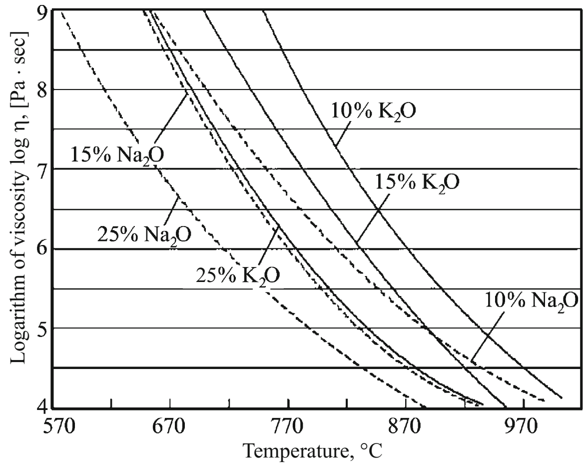

Fig. 2. Temperature dependences of the viscosity of glasses in the systems R_2O–B_2O_3–SiO_2 with 10% B_2O_3.

TABLE 1. Physical-Chemical Characteristics of Glasses

Composition No.	Refractive index	CLTE $\alpha \times 10^7$, K^{-1}	Composition No.	Refractive index	CLTE $\alpha \times 10^7$, K^{-1}
1k	1.5015	66.51	1n	1.5030	55.98
2k	1.5123	84.51	2n	1.5145	70.93
3k	1.5007	63.49	3n	1.5022	53.48
4k	1.5185	94.18	4n	1.5215	88.31
5k	1.5145	79.72	5n	1.5170	64.91
6k	1.4936	58.24	6n	1.4951	47.65
7k	1.5163	100.49	7n	1.5200	97.58
8k	1.5108	85.84	8n	1.5137	75.82
9k	1.5050	75.09	9n	1.5073	60.44
10k	1.4898	52.07	10n	1.4890	43.00

pansion coefficient (CLTE) was found using a DIL-402 dilatometer from the Netzsch Co. (Germany).

The refractive index of the experimental borosilicate glasses varies in the range 1.4890 – 1.5215. To secure the required numerical aperture of the optical fiber $A > 1$ the refractive index of the glass used for the light-reflecting cladding must not exceed 1.50, which is achieved with 10% R_2O.

The CLTE of glass must fall into the range $(60 - 65) \times 10^{-7}\ K^{-1}$ for the light-reflecting cladding of optical fiber and $(76 - 77) \times 10^{-7}\ K^{-1}$ for the protective cladding. CLTE in the range $(60 - 77) \times 10^{-7}\ K^{-1}$ is obtained with 10 – 15% K_2O and 15 – 20% Na_2O.

The temperature dependence of the glass viscosity in the range $10^{10} - 10^4$ Pa · sec was determined by compressing a continuous glass cylinder using a PPV-1000 viscosimeter from the Orton Company (USA). The error of determination is 1 – 2%.

The temperature dependences of the viscosity of glass with 10% B_2O_3 are presented in Fig. 2.

As the content of the alkali metal oxide replacing SiO_2 increases, the viscosity consistently decreases. For the same molar content of R_2O the viscosity of sodium glass is one or two orders of magnitude lower than that of potassium glass; the difference increases with decreasing temperature and with a transition from the liquid to the plastic state of the glassy material. Sodium glasses are distinguished by a smaller viscosity gradient. Thus, for 10% R_2O the temperature range of viscosity from 10^9 to 10^4 Pa · sec is 343°C for sodium glass and 254°C for potassium glass, while for 25% R_2O the ranges are 319 and 284°C, respectively. As the molar content of the alkali metal oxides increases, the difference in the viscosity gradient becomes smaller. It is pointed out in [3] that a fast and monotonic decrease of the viscosity is observed with small additions of alkali metal oxides, while with a more than 10 – 20% increase in the molar content of an oxide of the type R_2O its effect on the viscosity becomes less pronounced.

The effect of replacing B_2O_3 with K_2O and 65% SiO_2 is illustrated in Fig. 3.

The viscosity gradient decreases with increasing Na_2O content in the experimental glass. Thus, the temperature range of viscosity variation from 10^9 to 10^4 Pa · sec is 259°C for glass with 15% Na_2O and 320°C for 25% Na_2O.

The viscosity of sodium glass above 10^5 Pa · sec decreases with increasing Na_2O content. The temperature dependence of the viscosity of glass with 10% Na_2O is interest-

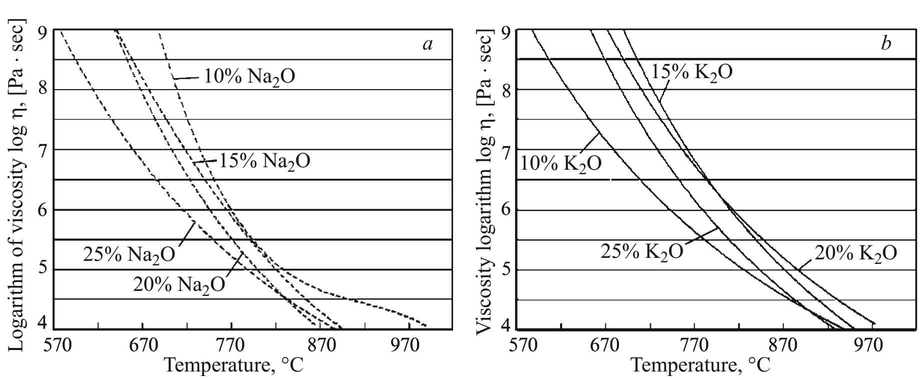

Fig. 3. Temperature dependences of the viscosity of glasses in the system R_2O–B_2O_3–SiO_2 with 65% SiO_2 content: sodium (*a*) and potassium (*b*) borosilicate glasses.

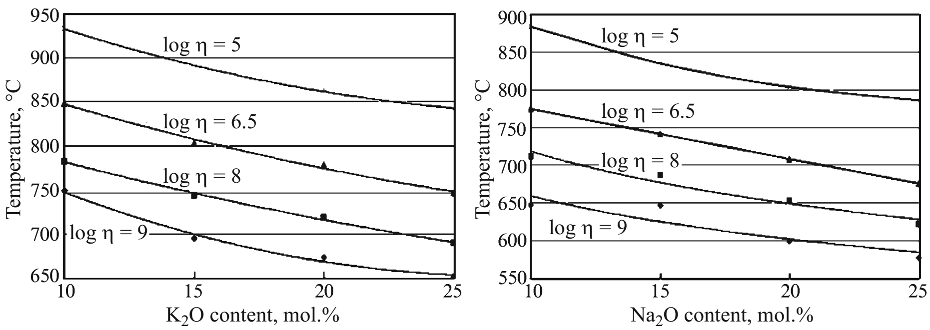

Fig. 4. Temperature versus the molar content of K_2O and Na_2O replacing SiO_2 for different values of the viscosity.

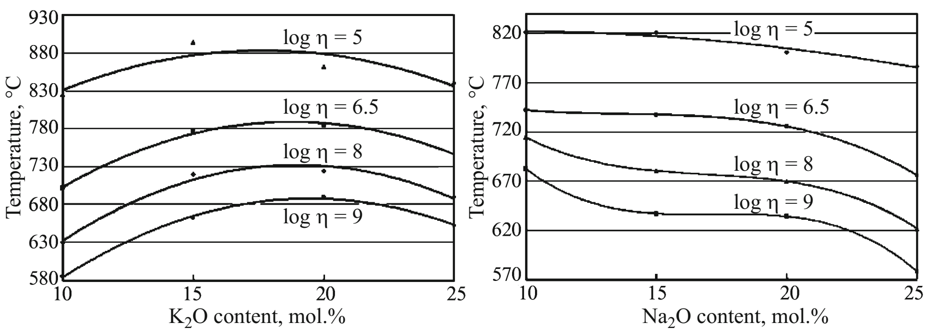

Fig. 5. Temperature versus the molar content of K_2O and Na_2O replacing B_2O_3 for different values of the viscosity.

ing. It is characterized by a sharp viscosity gradient and a change in the character of the dependence in the temperature range above 800°C. Since the B_2O_3 content is 25% in this case, it must be assumed that phase separation of the liquation type affects the viscosity curve.

As shown in [4], liquid phase separation, which develops during heat-treatment of glass with elevated B_2O_3 content, results in higher viscosity in the range $10^{10} - 10^4$ Pa · sec.

In contrast to sodium glasses, no clear increase of viscosity with increasing K_2O content is observed in the temperature dependence of the viscosity of potassium glasses: the lowest values of the viscosity are characteristic for glasses with 10% K_2O, especially in the range above 10^6 Pa · sec. Glasses with 15% K_2O are characterized by a larger viscosity gradient than glass with 20% K_2O.

A subsequent increase of the K_2O content results in an order of magnitude decrease of the viscosity. The largest difference in the viscosity of glass with different K_2O content appears at lower temperatures, corresponding to the plastic state. As temperature increases the viscosity curves converge, i.e., in the range of the liquid state of the glassy material the effect of the concentration factors on the viscosity of potassium glass is less pronounced.

It can be concluded on the basis of the temperature dependences of the viscosity of the experimental glasses that the effect of the concentration factor in the liquid state is much weaker than in the plastic state. The temperature corresponding to viscosity 10^4 Pa · sec is 60 – 80°C lower for sodium borosilicate glass than for potassium glass.

Curves of the temperature versus the content of the alkali metal oxides replacing SiO_2 for different constant values of the viscosity (isokomes) are presented in Fig. 4.

It follows from Fig. 4 that at temperatures below the Littleton temperature the viscosity changes by a proportional amount with increasing alkali metal content, i.e., at a transition from a fluid into a plastic state. For viscosity below $10^{6.5}$ Pa · sec a pronounced change of the indicators occurs with molar content of the components varying from 10 to 15%; subsequent increases of the alkali metal oxide content have a much weaker effect on the viscosity.

Curves of the temperature versus the content of alkali metal oxides replacing B_2O_3 at different constant values of the viscosity (isokomes) are presented in Fig. 5. The character of the dependences is determined by the molar ratio R_2O/B_2O_3 in the experimental glasses.

It can be concluded from the temperature curves for glasses with different K_2O content replacing B_2O_3 that the fluxing effect of potassium oxide is much weaker than that of boron oxide. The isokomes versus the K_2O content have maxima at ratio K_2O/B_2O_3 close to 1. As the ratio K_2O/B_2O_3 increases the fraction of $[BO_{4/2}]K$ groups increases. As these groups enter into association with tetrahedral groupings $[SiO]_{4/2}$ the degree of connectedness of the structural groupings increases and, correspondingly, the effect of the alkali metal on the viscosity of the experimental glasses becomes less active.

As a rule, the substitution of Na_2O for B_2O_3 in the experimental concentration ranges decreases viscosity. However, the effect of an alkali metal oxide is also determined by the

ratio Na_2O/B_2O_3; it is most pronounced at temperatures above the Littleton temperature (log η = 6.6).

The most active decrease of viscosity with increasing Na_2O content is observed with $Na_2O/B_2O_3 < 0.7$. As this ratio increases to 1.3 the substitution of Na_2O for B_2O_3 has virtually no effect. This is due to the fact that the content of the groupings $[BO_{4/2}]Na$ reaches a maximum when the ratio Na_2O/B_2O_3 is close to 1 and, in consequence, the internal friction increases as a result of the formation of borosilicon-oxygen groupings.

In summary, it was found that the effect of concentration factors on the temperature dependence of the viscosity of glasses in the system $K_2O–B_2O_3–SiO_2$ is complicated. Boron oxide shows a more pronounced fluxing action for viscosity above the Littleton point than potassium oxide, and the ratio K_2O/B_2O_3 affects the temperature dependence. The temperature dependences found for the viscosity make it possible to pick glass composition with a wide temperature range of viscosity variation $10^9 – 10^4$ Pa · sec, which is important in the technology of rigid optical fiber production.

REFERENCES

1. M. V. Dyadenko and I. A. Levitskii, "Glass for obtaining rigid optic fibers," *Steklo Keram.*, No. 5, 31 – 37 (2010); M. V. Dyadenko and I. A. Levitskii, "Glass for obtaining rigid optic fibers," *Glass Ceram.*, **67**(5 – 6), 152 – 157 (2010).
2. M. V. Dyadenko, I. A. Levitskii, and L. F. Papko, "Glass for optical fiber core of multistrand light guides," in: *Abstracts of Reports at the 7th International Conference of Young Scientists and Specialists, Optics-2011, St. Petersburg, October 17 – 21, 2011* [in Russian], St. Petersburg State University of Information Technology, Mechanics and Optics, NIUITMO, St. Petersburg (2011), pp. 42 – 44.
3. J. Shelby, *Glass Structure, Properties and Technology* [Russian translation], Mir, Moscow (2006).
4. I. A. Levitskii and L. F. Papko, "Effect of composition and structural factors on the viscosity of borosilicate glasses and melts," *Steklo Keram.*, No. 11, 4 – 7 (2010); I. A. Levitskii and L. F. Papko, "Effect of composition and structural factors on the viscosity of borosilicate glasses and melts," *Glass Ceram.*, **67**(11 – 12), 336 – 339 (2011).